Epitaxial Transition from Gyroid to Cylinder in a Diblock Copolymer Melt

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ジブロックコポリマーが形成するジャイロイド構造 (G) に、G ユニットセルの [111] 方向へのずり流動が課され、シリンダー構造 (C) へエピタキシャル転移する過程が実空間における動的 SCF 法でシミュレーションされた。構造変化を正確にシミュレートするために、システム・サイズ最適化法が導入された。転移の過程で、G 構造の中に C 構造の核形成が観察された。C 構造のエピタキシャル成長は、G 構造の 220 面が C 構造の 10 面に一致することがわかった。これは、G 構造の 211 面が C 構造の 10 面に一致するという、波数空間での理論計算の結果と実験的な観測結果と異なる。ずり流動の速度勾配の方向を変えると、C 構造が生成せず、G 構造が分割・合体を繰り返すこともわかった。したがって、G 構造から C 構造へのエピタキシャル転移の動力学は、格子定数の一致だけでなく速度勾配の方向にも依存するといえる。

1 Introduction

In the past, the self-organized microdomain structures of diblock copolymers have been the target of extensive studies both experimentally and theoretically. Among various microdomain structures, the bicontinuous double gyroid (G) structure has attracted a great interest because of its complex but highly symmetric structure. We simulated an order-order transition from a G structure to a hexagonally packed cylinder (C) structure induced by an external flow in [111] direction of the G unit cell using real-space dynamical self-consistent field technique. In order to simulate the structural change correctly, we introduce a system size optimization (SSO) technique by which emergence of artificial intermediate structures are suppressed.

2 SSO method

To obtain equilibrium states of the periodic microdomain structures of G and C, we regard the side length of the simulation box $\mathcal{L}_i$ $(i = x, y, z)$ as a dynamical variable whose dynamics is described by the following ficticious equation of motion

$$\frac{\partial \mathcal{L}_i}{\partial t} = -\zeta_i \frac{\partial (\mathcal{F}/\mathcal{V})}{\partial \mathcal{L}_i}, \tag{1}$$

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where $(\mathcal{F}/\mathcal{V})$ is the free energy density and ζ_i is a positive coefficient. We checked the validity of this equation and found that the most appropriate value of the ζ_i is 0.05 for the C phase ($\chi N = 15$, block ratio $f = 0.35$).

3 Results and Discussion

The temporal change of the G periodic cell under a shear flow to the [111] direction and a sudden temperature change from $\chi N = 20$ to $\chi N = 15$ is shown in Fig. 1. The G structure is deformed by the shear flow as shown in Figs. 1(a) and 1(b). A small domain of cylinders is generated in Fig. 1(c), which is indicated by an open arrow. The transition from the G structure to the C structure takes place at the lower grain boundary of this C domain as shown in Figs. 1(d)-(f). This transition reproduces a nucleation of the C domains. The generated C domains grow epitaxially, where the {220} planes of the G structure coincide with the {10} planes of the C structure (so called epitaxial growth) as Fig. 2., while the theoretical studies in reciprocal space and the experimental studies suggest {211} to {10} transition [1].

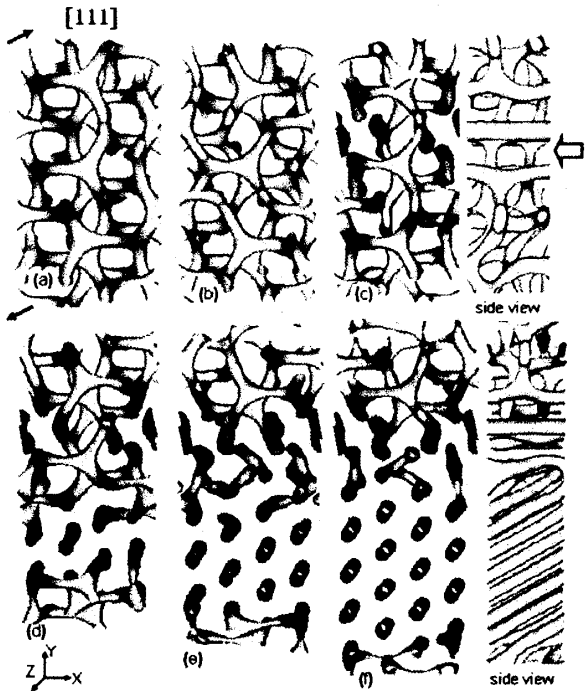

Fig. 1 Time evolution of the domain in the OOT G → C.

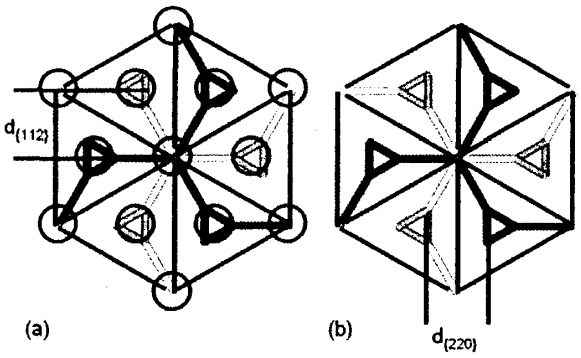

Fig. 2 Projection of the G unit cell structure observed from the [111] direction. The circles indicate the positions of the cylindrical domains in the epitaxial transition (a) G {211} → C{10} and (b) G {211} → C{10}, respectively.

References

[1] T. Honda and T. Kawakatsu, Macromolecules. **39** (2006), 2340.